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(54) Membrane-covered electrochemical gas sensor

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DE 297 09 141 U1

Membrane-Covered Electrochemical Gas Sensor

Purpose of the Invention

The invention concerns a membrane-covered electrochemical gas sensor according to the Severinghaus principle, especially a sensor to measure the carbon dioxide content in gases, especially in the air.

State-of-the-art

Membrane-covered potentiometric gas sensors that function according to the Severinghaus principle are constructed in the following familiar manner:

- A pH combined electrode is disposed inside a cylindrical sensor shaft or sensor housing so that the measuring surface responding to changes in pH, termed "H^+-sensitive" measuring surface in the following, extends into an opening that is on the bottom face of the shaft or housing.
- Drawn across this opening is a liquid-tight, gas-permeable polymer membrane that completely covers the H^+-sensitive measuring surface.
- The sensor shaft or housing is filled with an electrolyte that reacts to the measure gas with a change in pH.
- The electrolyte filling in the sensor shaft or housing forms a thin layer between the gas-permeable polymer membrane and the H^+-sensitive measuring surface, and its thickness is defined by a spacer material that minimally restricts gas diffusion.

To measure the change in pH that is a function of the logarithm of the change in partial pressure of the measured gas, glass electrodes are generally preferred over other H^+-sensitive electrodes even though they are brittle since they last longer, and the measured values change less over time.

This sensor principle is generally used for gases that diffuse through the polymer membrane and cause a change in the pH of the electrolyte that is clearly related with the

gas concentration. Except in sensors for NH_3 and SO_2, this principle is primarily used for measuring the CO_2 partial pressure in liquids and gases, especially in air.

The use of a glass electrode with a lens-shaped glass membrane on the front of a glass tube also determines the external shape of the CO_2 sensor that is usually designed as a cylindrical rod with a gas-permeable membrane at the bottom end. This rod shape that is advantageous for measuring liquids, especially for installing the sensor in a container or a flow measuring cell, is disadvantageous when gases are measured. For this use, robust drum-shaped compact designs 10-30 mm in diameter and 10-30 mm high are preferred which are either inserted and held in a corresponding sleeve and hence can be easily exchanged, or are soldered to printed circuit boards of electronic measuring devices.

Such a compact sensor for CO_2 according to the Severinghaus principle forms the basis of unexamined patent application DE 19515065 and is described in greater detail with reference to Fig. 1.

The compactly designed CO_2 sensor consists of a round, flat plastic housing and a removable epoxide resin top part that is affixed to the sensor housing and is sealed against the electrolyte by means of a union nut and O-ring. It serves as a holder for the glass pH combined electrode. A platinum coating on the outside surface of the glass electrode shaft is required to hold to the greatly-shortened pH combined electrode in the epoxide resin body so that it is electrolyte-tight. It forms the basis for the Ag/AgCl reference electrode. The gas diffusion membrane made of a polymer material that is affixed to the sensor housing with an O-ring is stretched across the lens-shaped pH-sensitive measuring surface of the glass electrode. Diluted hydrogen carbonate solution is used as the electrolyte filling that forms a thin layer between the pH-sensitive measuring surface and the polymer membrane whose thickness is determined by the utilized spacer material.

A membrane protective ring with a metal grid that is held by a union nut protects the mechanically sensitive part of the sensor.

The CO_2 sensor can be regenerated by changing the polymer membrane and refreshing the electrolyte filling.

Problem

The glass electrode of the pH combined electrode is filled with buffer solution. It cannot however be completely filled, i.e. without an air bubble. Because it is made out of blown glass, an air gap remains in the top part of the glass shaft because the inner terminal lead in the glass electrode is sealed in after the buffer solution is added, and a corresponding distance to the site of fusion must be maintained to keep the buffer solution from evaporating. In addition, completely filling the glass electrode with buffer solution without an air bubble would cause the H^+-sensitive glass membrane to burst when the temperature changes because the expansion coefficients of the glass body and buffer solution differ by at least a power of 10.

When filling the sensor with the hydrogen carbonate electrolyte, there also has to be an air bubble in the electrolyte space between the sensor housing and pH combined electrode to compensate for pressure.

When screwing the union nut tight, the epoxide resin top part is also slightly pressed into the sensor housing after mounting the O-ring on the sealing surface. Filling the sensor with electrolyte without an air bubble would cause the polymer film to expand and rise off the H^+-sensitive measuring surface since the electrolyte filling can only escape in this direction.

Both of these facts mean that the function of the CO_2 sensor depends on location. The sensor can only operate properly up to a deviation of 90° from a vertical position. If the angle increases or the sensor is upside down, there is a danger that the air bubble inside the glass electrode will migrate upward through the buffer filling and prevent the glass membrane from being fully covered with buffer solution.

When the sensor is upside down, the air bubble in the electrolyte filling can enclose the glass electrode in a ring shape directly after the polymer membrane and hence prevent or even interrupt the contact of the thin electrolyte layer between the polymer membrane and the H^+-sensitive measuring surface to the reference electrode of the pH combined electrode.

In both cases, the sensor will not function properly.

Invention

This problem is solved by the measures in claims 1 and 2.

Description of the invention

An exemplary embodiment of the invention will be explained with reference to Fig. 1. Fig. 1 shows a compact design of the membrane-covered electrochemical gas sensor according to the Servinghaus principle with the features according to the invention.

Fig. 1 shows a membrane-covered electrochemical gas sensor consisting of an epoxide resin body A with a pH combined sensor B cast and thereby affixed in this body, and the combined sensor is inserted in a sensor housing made of plastic C, is held tightly by the union nut D1 and an O-ring C1 against the sensor housing. A polymer membrane C2 held by the O-ring C3 seals the floor opening of the sensor housing and stretches across the lens-shaped, H^+-sensitive measuring surface B1 of the pH combined electrode B. A thin layer of electrolyte filling C4 is enclosed between the H^+-sensitive measuring surface B1 of the glass electrode and the polymer membrane C2, and is stabilized by the spacer material C5. The membrane protective ring E whose opening is covered with a perforated plate E1 and is affixed with a union nut D2 to the sensor housing C protects the sensitive parts of the sensor from mechanical destruction.

The pH combined electrode B consists of the H^+-sensitive glass membrane B1, the Ag/AgCl reference electrode B2, the sealed-in the inner tube B3 with the Ag/AgCl terminal lead B4, and at the temperature sensor B5. The interior of the glass electrode is filled with buffer solution B6 without any air bubbles. At the top end of the glass shaft, a side tubular section B7 is melted on whose transition to the interior of the glass electrode is narrowed like a capillary (B8). An air bubble B9 is held in the side tubular section B7 by the capillary restriction B8 outside of the buffer filling of the glass electrode and cannot impair the glass electrode's function when its position changes, but is sufficient to compensate for the different thermal expansions of the glass body and buffer solution when the temperature changes. The side tubular section B7 is usefully at the height of the shoulder A1 in the epoxide resin body A to allow the side tubular section to be sufficiently long.

In Fig. 1, there is a hollow plug C6 made of an elastic material in a hole in the shoulder of the sensor housing C, and the middle of the hollow plug is designed as a septum. This septum enables the sensor housing covered with the membrane to be filled with the hydrogen carbonate electrolyte without an air bubble, and the pressure is compensated through a small-lumen syringe cannula that penetrates the septum during the filling process.

The length of the glass shaft of the pH combined electrode B is such that the edge of the lens-shaped H^+-sensitive measuring surface B1 extends beyond the edge of the opening of the sensor housing C as shown in Fig. 1 so that the polymer membrane C2 lifts from its contact surface with the sensor housing and forms a movable side C7 that compensates for the different thermal expansions of the glass body, plastic housing and electrolyte filling when the temperature changes.

Advantages of the invention

The compact, membrane-covered electrochemical gas sensor according to the invention that is based on the Severinghaus principle and specially designed as a CO_2 sensor can be

used in different positions. The invention is applicable for all compact membrane-covered gas sensors that function according to the Severinghaus principle.

A sensor manufactured according to the features of the invention, for example to measure CO_2 concentration, is particularly suitable for use in safety technology because it can be installed in a portable CO_2 measuring and warning device even when one cannot ensure that the device will always be operated in a specific, predetermined position.

Claims

1. Membrane-covered electrochemical gas sensor according to the Severinghaus principle in a compact design, consisting of an epoxide resin body (A), a glass pH combined sensor (B) sealed in this body, and a sensor housing (C) consisting of plastic whose bottom opening is covered with a polymer membrane (C2) that is connected electrolyte-tight to the epoxide resin body, is filled with an electrolyte solution (C4), and is disposed in the pH combined electrode so that the polymer membrane covers the H^+-sensitive measuring surface (B1) of the glass electrode while forming a thin layer of the electrolyte solution stabilized by a spacer material (C5), whereby

- at the top end of the shaft of the glass electrode, a side glass tubular section (B7) is welded on whose part abutting the inside of the shaft is narrowed like a capillary, the interior of the shaft of the glass electrode is filled with the internal buffer without an air bubble up to the narrowing (B8), and an air bubble (B9) is enclosed at the end of the glass tubular piece by melting the glass closed,
- in a radial hole in the shoulder of the sensor housing C, there is a hollow plug (C6) with a septum in the middle,
- the shaft of the glass pH combined electrode (B) extends out of the bottom opening in the sensor housing C enough for the polymer membrane (C2) stretched over the H^+-sensitive measuring surface (B1) to lift from the side contact surface of the sensor housing and form a movable side (C7).

2. Membrane-covered electrochemical gas sensor according to the Severinghaus principle in a compact design according to 1, whereby the glass combined electrode (B) is disposed in the epoxide resin body (A) such that the side tubular section (B7) is at the height of the shoulder (A1).

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CERTIFICATION OF ACCURACY

I CERTIFY, UNDER PENALTY OF PERJURY UNDER THE LAWS OF THE UNITED STATES OF AMERICA THAT WE ARE COMPETENT IN **ENGLISH** AND **GERMAN** AND THAT THE FOLLOWING IS, TO THE BEST OF OUR KNOWLEDGE AND BELIEF, A TRUE, CORRECT, COMPLETE AND ACCURATE TRANSLATION OF THE **DOCUMENT REGARDING PATENT DE 271 09 141 U1.**

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